

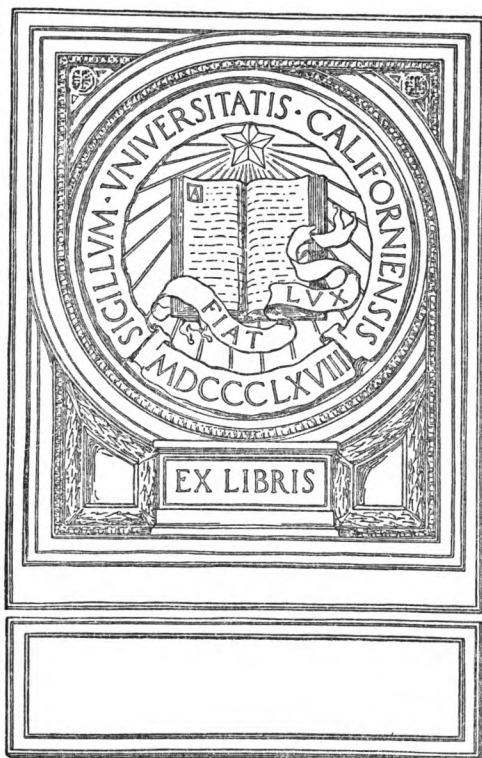
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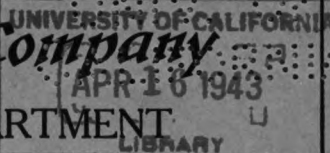


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# THE CRYSTAL STRUCTURES OF POTASSIUM AND BERYLLIUM

BY

L. W. McKEEHAN

TWO ELEMENTS  
ARE ADDED TO THE LIST OF THOSE WITH KNOWN STRUCTURES  
AND ARE OF THE STRUCTURAL TYPES TO BE EXPECTED.  
RELATIONS BETWEEN BERYLLIUM AND ITS OXIDE EMPHASIZED



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## THE CRYSTAL STRUCTURE OF POTASSIUM

By L. W. MCKEEHAN

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AND THE WESTERN ELECTRIC COMPANY, INCORPORATED.

Communicated June 13, 1922

Potassium, when examined by X-rays at room temperature appears to be amorphous, as previously reported by Hull.<sup>1</sup> But if potassium, cast in a thin-walled cylindrical glass tube, is cooled to  $-150^{\circ}\text{C}$ . in a current of air by the method recently employed in getting the crystal structure of mercury,<sup>2</sup> large crystals, giving well marked reflections of the K-radiation of molybdenum, are formed. These crystals are, in fact, so large that it is a matter of some difficulty to obtain enough different orientations in a single sample, and the data are not of great accuracy. Continuous rotation of the sample about the axis of the cylinder so weakens the intensity of the occasional reflections that they can no longer be located with certainty. The best results are obtained by rotating the sample through small angles at such long time-intervals that individual crystals in suitable orientations have long enough to affect the film.

The best fit with the data is furnished by assuming the atoms to be arranged in a body-centered cubic lattice with  $a = 5.20 \times 10^{-8}$  cm. and therefore with a density 0.92 gm./cm.<sup>3</sup> This density is higher than the commonly accepted value, 0.862 gm./cm.<sup>3</sup>, partly no doubt on account of the low temperature of the crystals, and partly perhaps because the values usually quoted have been obtained for metal not perfectly crystalline, to judge by the X-ray evidence. As regards the purity of the potassium here used, it can only be stated that the original material was purchased as "c. p." from Eimer and Amend, was dried and freed from the usual oily surface layer, and was then melted and double-distilled in vacuo using only pyrex glass. The samples were prepared for me under the supervision of Dr. H. E. Ives from material used by him in the preparation of photoelectric cells. His suggestion that a change in the crystalline

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condition of the metal at low temperatures might be responsible for certain anomalies in photoelectric emission was the starting point of this research. The observed crystalline structure does not persist when the temperature is allowed to rise again to about 20° C. No effort has been made to determine the highest temperature at which crystallinity can still be detected, since it seems probable that the loss of structural symmetry is not abrupt but gradual.

<sup>1</sup> A. W. Hull, *Physic. Rev.*, (2) **10**, 661-696 (Dec., 1917).

<sup>2</sup> L. W. McKeehan and P. P. Cioffi, *Ibid.*, (2) **19**, 444-446 (April, 1922).

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*THE CRYSTAL STRUCTURE OF BERYLLIUM AND OF  
BERYLLIUM OXIDE*

By L. W. McKEEHAN

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Communicated July 17, 1922

The structure of the lighter elements and of their compounds should, on account of their greater simplicity, be of especial value in deciding what rôle the so-called valence electrons play in connecting atoms. Beryllium (Be; atomic number 4) is the lightest metal the crystal structure of which has not hitherto been determined by X-ray methods. Its accepted atomic weight is  $w = 9.10$ , although a recent determination,<sup>1</sup> apparently of high accuracy, gives  $w = 9.018$  which is in much better agreement with the

evidence indicating that the element consists of a single atomic species.<sup>2</sup>

Through the kindness of one of my colleagues, Dr. H. E. Ives, a small supply of metallic beryllium, recently prepared for him in this laboratory by Mr. G. O. Smith, was made available to me for this study. The method of preparation was by the electrolysis of  $2\text{BeF}_2 \cdot \text{NaF}$  with from 7 to 15 amperes at 80 volts. This is a modification of the method of Fichter and Jablczynski<sup>3</sup> who used a lower voltage. The product of the process is a fine gray powder interspersed with thin flakes up to half a millimeter in greatest dimensions, which show good metallic lustre. The principal impurity to be expected is beryllium oxide ( $\text{BeO}$ ), and this should not exceed in amount a few per cent by weight.

A thin-walled pyrex glass tube about one millimeter in diameter was packed loosely with the beryllium powder, the looseness of packing being intended to reduce the chance of anisotropy.<sup>4</sup> This sample was not thick enough to cast a very sharply defined shadow on the film, a circumstance which somewhat reduces the accuracy of the results.<sup>5</sup> A water-cooled molybdenum target, bombarded by about 30 milliamperes of electrons at about 30,000 volts, and provided with  $\text{ZrO}_2$  filters<sup>6</sup> gave an intense source of X-rays, the photographically important wave-lengths being<sup>7</sup>  $0.71212 \times 10^{-8}$  cm. ( $\text{K } \alpha_2$ ) and  $0.70783 \times 10^{-8}$  cm. ( $\text{K } \alpha_1$ ). The radius of the photographic film was 20.36 cm. The time of exposure was about 18 hours. In taking the first photograph the cylindrical sample was kept stationary; in taking the second photograph the sample was rotated about its axis through a small angle at intervals of one hour. The two photographs were quite similar in general appearance, but the second had smoother lines in its pattern, so that it alone was used in the final measurements and calculations.

In order to eliminate from consideration any lines certainly due to the presence of  $\text{BeO}$  a sample of that substance in the form of a fine powder was examined in the same way. The results are presented in Table I, and show that the diffracting centers lie at the points of two symmetrically interpenetrating hexagonal space lattices, each with the axial ratio  $c/a = 1.63$  and with  $a = 2.696 \times 10^{-8}$  cm. There are three faint lines which must be attributed to the presence of impurities. Assuming that one molecule,  $\text{BeO}$ , is associated with each lattice point and taking<sup>8</sup>  $N = 6.0594 \times 10^{23}$ ,  $w = 9.018$ , this gives a computed density 2.99 gm./cm<sup>3</sup>. Both structure and density are in agreement with published values,<sup>9</sup> although a recent paper by Gerlach<sup>10</sup> contains a very different result. A careful examination of his data, however, shows that the resolving power of his apparatus was not high, and that all the lines which he reported as intense are within a short distance of positions accountable for by the structure here proposed.



Comparing the pattern obtained for Be with that obtained for BeO it was found that the first three lines in the former and possibly also the fourth were attributable to the oxide and its principal impurity. A brief search by graphical methods<sup>11</sup> showed that the fundamental space lattice was hexagonal, and that the fourth line of pattern might be retained. A more exact analysis gives the results presented in Table II, and shows that the diffracting points form two symmetrically interpenetrating hexagonal lattices, each with the axial ratio  $c/a = 1.58$  and with  $a = 2.283 \times 10^{-8}$  cm. No lines are left unaccounted for this structure, which is consistent with the hexagonal structure ( $c/a = 1.5802$ ) determined by optical methods.<sup>12</sup> Assuming that one atom is associated with each lattice point, and taking  $N$  and  $w$  as given above, this gives a computed density  $1.827$  gm./cm<sup>3</sup>., or about one per cent less than the best previous values.<sup>13</sup> The relative positions of the two component space lattices along the hexagonal axis are not determined with any accuracy, the intensities being very roughly estimated and not particularly significant.

Comparing the proposed structure for Be with those already reported for elements in the same column of the periodic table, it is clear that it belongs rather with Mg, Zn, and Cd than with Ca, Sr, and Ba, the first three being hexagonal, all with  $c/a$  greater than 1.58 and increasing with the atomic

TABLE I—Be

ESTIMATED INTENSITY	MEASURED 2 $\theta$ IN CM.	COMPUTED LOG (10 <sup>4</sup> d)	ATTRIBUTED TO <sup>1</sup>	COMPUTED <sup>2</sup> LOG (10 <sup>4</sup> a)
2	4.69	0.4911	X <sup>3</sup>	
6	6.60	0.3437	BeO	
1	6.97	0.3201	BeO	
4	7.44	0.2921	(10.0)	0.3546
2	8.05	0.2583	(00.2)	0.3607
10	8.37	0.2416	(10.1)	0.3611
2	11.02	0.1244	(10.2)	0.3587
4	12.89	0.0583	(11.0)	0.3593
2	14.44	0.0108	(10.3)	0.3576
	"		(20.0)	
	"		(11.2)	
2	15.55	1.9801	(20.1)	0.3593
	"		(00.4)	
	"		(20.2)	
1	18.33	.9128	(10.4)	0.3572
			Mean	0.3586
			Result $a =$	$2.283 \times 10^{-8}$ cm.

<sup>1</sup> All planes theoretically capable of reflection within the range of the tabulated values of  $2\theta$  are included.

<sup>2</sup> Computed for  $c/a = 1.58$ .

<sup>3</sup> X = impurity in BeO.

<sup>4</sup> Diffuse band not resolved. The theoretical range in  $2\theta$  is only 0.58 cm.

<sup>5</sup> Not observed with certainty.

number, whereas Ca, the only member of the second three which has been analyzed, has cubic symmetry.<sup>14</sup> The remaining element in this column, Hg, has rhombohedral symmetry.<sup>15</sup>

The oxide, BeO, finds an analog in ZnO, all the other monoxides in the column having cubic symmetry,<sup>16</sup> except HgO which forms monoclinic crystals.<sup>17</sup> The structure of ZnO has been reported by W. L. Bragg<sup>18</sup> to be hexagonal close-packing of molecules with  $c/a = 1.608$  and  $a = 3.22 \times 10^{-8}$  cm. Recent data obtained by Hedvall<sup>19</sup> but not reduced by him is in good agreement with this structure. Bragg regards the two hexagonal lattices of the proposed arrangement as determining the positions of the zinc atom-centers, and suggests that the oxygen atom-centers lie at the points of two similar lattices derived from these by displacing both of them along the hexagonal axis by about  $3c/8$ . The same type of structure is at

TABLE II—BeO

ESTIMATED INTENSITY	MEASURED $2\theta$ IN CM.	COMPUTED LOG (10 <sup>4</sup> d)	ATTRIBUTED TO <sup>1</sup>	COMPUTED <sup>2</sup> LOG (10 <sup>4</sup> a)
2	4.69	0.4911	$\bar{Y}^3$	
1	5.43	0.4277	X	
8	6.23	0.3685	(10.0)	0.4310
6	6.67	0.3392	(00.2)	0.4301
10	7.09	0.3128	(10.1)	0.4297
1	7.57	0.2847	X	
3	9.15	0.2035	(10.2)	0.4311
8	10.90	0.1290	(11.0)	0.4300
8	11.89	0.0923	(10.3)	0.4308
	4		(20.0)	
6	12.86	0.0593	(11.2)	0.4303
	4		(20.1)	
	4		(00.4)	
	4		(20.2)	
	4		(10.4)	
2	16.40	$\bar{I}.9582$	(20.3)	0.4293
1	16.90	$\bar{I}.9459$	(21.0)	0.4309
1	17.29	$\bar{I}.9366$	(21.1)	0.4303
	4		(11.4)	
	4		(10.5)	
2	18.34	$\bar{I}.9126$	(21.2)	0.4304
	4		(20.4)	
1	19.35	$\bar{I}.8911$	(30.0)	0.4305
2	20.04	$\bar{I}.8770$	(21.3)	0.4298
			Mean	0.43032
			Result $a =$	$2.696 \times 10^{-8}$ cm.

<sup>1</sup> All planes theoretically capable of reflection within the range of the tabulated values of  $2\theta$  are included.

<sup>2</sup> Computed for  $c/a = 1.63$ .

<sup>3</sup> X = impurity.

<sup>4</sup> Not observed with certainty.

<sup>5</sup> Forms with next an irresolvable doublet ( $\Delta s = 0.01$  cm.).

least consistent with the data for BeO. In both cases there should be different properties in the two directions of the hexagonal axis.

The fact that  $c/a$  is greater for Zn than for Be, but less for ZnO than BeO is hard to explain unless we assume a considerable rearrangement of electrons to take place during the formation of one of the oxides. It is interesting to note that another substance which possesses this structure is ice,<sup>20</sup> which tempts one to regard frozen water as an oxide of the formula  $(OH_4)O$ , the radical  $OH_4$  being divalent, just as  $NH_4$  is univalent and  $CH_4$  is saturated.

<sup>1</sup> O. Hönigschmidt and L. Birckenbach, *Ber. deut. chem. Ges.*, **55**, 1922 (4-12).

<sup>2</sup> G. P. Thomson, *Phil. Mag.*, (6) **42**, 1921 (857-867).

<sup>3</sup> F. Fichter and K. Jablczynski, *Ber. deut. chem. Ges.*, **46**, 1913 (1604-1611); J. S. Negru, *Chem. and Met. Eng.*, **21**, 1919 (353-359).

<sup>4</sup> M. Polanyi, *Z. Physik.*, **7**, 1921 (149-180).

<sup>5</sup> L. W. McKeehan, *Frank. Inst. J.*, **193**, 1922 (231-242).

<sup>6</sup> W. P. Davey, *Opt. Soc. Amer. J.*, **5**, 1921 (479-493).

<sup>7</sup> W. Duane, *Nat. Res. Council. Bull.*, **1**, 1920 (383-406).

<sup>8</sup> R. T. Birge, *Physic. Rev.*, (2) **14**, 1919 (361-368).

<sup>9</sup> P. Groth, *Chemische Kristallographie*, Leipzig, **1**, 1906. C. L. Parsons, *The Chemistry and Literature of Beryllium*, Easton, Pa., 1919.

<sup>10</sup> W. Gerlach, *Z. Physik.*, **9**, 1922 (184-192).

<sup>11</sup> A. W. Hull and W. P. Davey, *Physic. Rev.*, (2) **17**, 1921 (549-570); W. P. Davey, *loc. cit.*

<sup>12</sup> P. Groth, *loc. cit.*

<sup>13</sup> C. L. Parsons, *loc. cit.*; F. Fichter and K. Jablczynski, *loc. cit.*

<sup>14</sup> A. W. Hull, (Mg) *Physic. Rev.*, (2) **10**, 1917 (661-696); (Ca) *Ibid.*, (2) **17**, 1921 (42-44); (Zn, Cd) *Ibid.*, (2) **17**, (571-588).

<sup>15</sup> L. W. McKeehan and P. P. Cioffi, *Ibid.*, (2) **19**, 1922 (444-446).

<sup>16</sup> (MgO) W. P. Davey and E. O. Hoffmann, *Ibid.*, (2) **15**, 1920 (333); R. W. G. Wyckoff, *Amer. J. Sci.*, (5) **1**, 1921 (138-152); (CaO, Sr, BaO) O. Gerlach, *loc. cit.*; (MgO, CaO, SrO, CdO, BaO) P. Groth, *loc. cit.*

<sup>17</sup> P. Groth, *loc. cit.*

<sup>18</sup> W. L. Bragg, *Phil. Mag.*, (6) **39**, 1920 (647-651).

<sup>19</sup> J. A. Hedvall, *Z. anorg. allg. Chem.*, **120**, 1922 (327-340).

<sup>20</sup> W. H. Bragg, *Phys. Soc. London Proc.*, **34**, 1922 (98-103).















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